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13. ABSTRACT (Maximum 200 words) The project goals are the synthesis of new materials having the potential for use as ion-conducting membranes. We have been able to make rugged membrane structures from a polymer of interest by first casting the polymer on a surface then exposing it to UV irradiation. These procedure generates free standing membranes that are quite durable in themselves. The initial goal has been to investigate the use of unsaturated carbosilane monomer functionalized with an Si-Cl bond in the synthesis of new materials for use as ion-conducting membranes. We've spent most of our time devising the synthesis chemistry needed to create chlorosilane monomers substituted with appropriate nucleophiles. The nucleophiles employed thus far have been diethylene glycol methyl ether and the sodium salt of 3-hydroxy-1-propane-sulfonic acid.				
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FINAL PROGRESS REPORT

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K.R. Brzezinska, Postdoctoral Associate
K. B. Wagener, Professor of Chemistry
J.R. Reynolds, Professor of Chemistry
9. **REPORTS OF INVENTIONS BY TITLE:** None

K.B. Wagener
Department of Chemistry
University of Florida
Gainesville, FL 32611

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Description of the research problem studied. Our work is related to the synthesis of new materials having the potential for use as ion-conducting membranes (Figure 1). These materials should be impermeable to methanol penetration or crossover; they should be able to transport protons with relative ease and they should have a high ion conductivity.

Summary of the most important results. The project goals are to investigate the use of unsaturated carbosilanes functionalized with a Si-Cl bond in the synthesis of new materials having the potential for use as ion-conducting membranes (Figure 1).

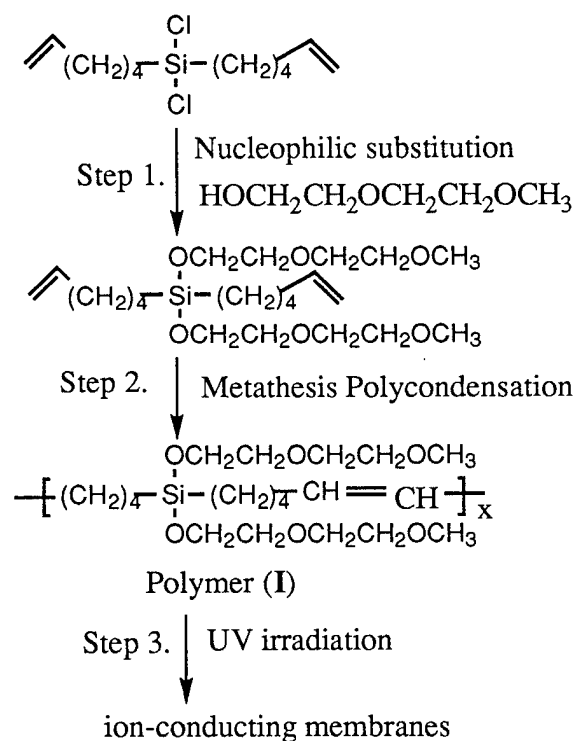


Figure 1. The synthesis of new materials having the potential for use as ion-conducting membranes.

We have been able to make rugged membrane structures from a polymer (I) by first casting the polymer on a surface then exposing it to UV irradiation. This procedure generates free standing membranes that are quite durable in themselves.

We've spent most of our time devising the synthesis chemistry needed to create chlorosilane monomers substituted with appropriate nucleophiles. The nucleophiles employed thus far have been diethylene glycol methyl ether and the sodium salt of 3-hydroxy-1-propane sulfonic acid. First the backbone monomer, dichlorodihexenylsilane (made for Doug Kiserow's elastomer project) was synthesized via hydrosilation chemistry. Nucleophilic substitution then was done on this monomer with the diethylene glycol methyl ether nucleophile (step 1, Figure 1). ADMET polymerization followed to give a highly viscous oil (step 2, Figure 1) and this oil was then converted into a membrane as described above (cast on surface, UV irradiation).

Nucleophilic substitution on the Si-Cl bond in the carbosilane monomer with sodium salt of 3-hydroxy-1-propane sulfonic acid produced a solid. This product was insoluble in organic solvents (toluene, chloroform) but soluble in DMF or DMSO. Substitution on the Si-Cl bond in the dichloro-carbosilane polymer with sodium salt of 3-hydroxy-1-propane sulfonic acid produced material insoluble in virtually every solvent system studied.

List of all publications and technical reports: None.

Scientific personnel supported by this project and degrees awarded during this period.

K.R. Brzezinska, Postdoctoral Associate
K.B. Wagener, Professor of Chemistry
J.R. Reynolds, Professor of Chemistry

Reports of invention by title. None.

Bibliography

1. "Acyclic Diene Metathesis Polymerization. The Olefin Metathesis Reaction of 1,5-Hexadiene and 1,9-Decadiene", M. Lindmark-Hamberg and K.B. Wagener, *Macromolecules*, **20**, 2949 (1987).
2. "The Key to Successful Acyclic Diene Metathesis Polymerization Chemistry", K.B. Wagener, J.M. Boncella, J.G. Nell, R.P. Duttweiler and M.A. Hillmyer, *Makromol. Chem.* **191**, 365 (1990).
3. "Acyclic Diene Metathesis Polymerization", K.B. Wagener, J.M. Boncella and J.G. Nel, *Macromolecules*, **24**, 2649 (1991).
4. "Acyclic Diene Metathesis (ADMET) Polymerization. The Synthesis of Unsaturated Polyethers", K. Brzezinska and K.B. Wagener, *Macromolecules*, **24**, 5273 (1991).
5. "Acyclic Diene Metathesis (ADMET) Polymerization. Synthesis of Unsaturated Polythioethers", J.E. O'Gara, J.D. Portmess and K.B. Wagener, *Macromolecules*, **26**, 2837 (1993), and references therein.
6. "Acyclic Diene Metathesis (ADMET) Polymerization Using a Well-Defined Ruthenium Based Metathesis Catalyst", K.R. Brzezinska, P.S. Wolfe, M.D. Watson, and K.B. Wagener, *Macromol. Chem. Phys.*, **197**, 2065 (1996).
7. "Inorganic and Organometallic Polymers (Macromolecules Containing Silicon, Phosphorus and Other Inorganic Elements)", M. Zeldin, K.J. Wynne, H.R. Allcock, Eds., American Chemical Society, Washington DC, 1988, and references therein.
8. "Silicon-Based Polymer Science", J.M. Ziegler and F.W. Gordon Fearon, Eds., American Chemical Society, Washington DC, 1990.
9. "Acyclic Diene Metathesis (ADMET) Polymerization. Synthesis and Characterization of Unsaturated Polycarbo-(dimethyl)silanes", D.W. Smith, Jr. and K.B. Wagener, *Macromolecules*, **24**, 6073 (1991).

10. "Acyclic diene Metathesis (ADMET) Copolymerization. Synthesis of poly(siloxaalkenylene-co-biphenylene)", D.W. Smith, Jr. and K.B. Wagener, *Polymer Preprints*, **33** (2), 112 (1992).
11. "Acyclic Diene Metathesis (ADMET) Depolymerization. Design and Synthesis of Unsaturated Polycarbosiloxanes", D.W. Smith, Jr. and K.B. Wagener, *Macromolecules*, **26**, 1633 (1993).
12. S. Cumings, E. Ginsburg, R. Miller, J. Portmess, D. Smith and K.B. Wagener "Step Growth-Polymers for High-Performance Materials: New Synthetic Methods", Eds., J.L. Hedrick and J.W. Labadie, ACS Symposium Series #624, Chapter 6, page 113 (1996).
13. "Synthesis and Characterization of a Chlorofunctionalized Unsaturated Carbosilane Oligomer", S.K. Cummings, D.W. Smith and K.B. Wagener, *Macromol. Rapid Commun.*, **16**, 347 (1995).
14. "The Synthesis and Characterization of Chlorofunctionalized Unsaturated Carbosilane Oligomers and Polymers", *Polymer Prepr.*, **36** (2), 162 (1995).
15. "Acyclic Diene Metathesis (ADMET) Polymerization. Thermal, UV and Chemical Modification of ADMET Polyethers", *Macromolecules*, **25**, 2049 (1992).
16. M.S. Wilson, J.A. Valerio and S. Gottesfeld, *Elektrochim. Acta.*, **40**, 355 (1995).
17. X. Ren, M.S. Wilson and S. Gottesfeld, *J. Electrochem. Soc.*, **143**, L12 (1996).
18. B. Scrosati, *Nature*, **373**, 557 (1995).
19. P.M.S. Monko, R.J. Mortimer and D.R. Rosseinsky, *Electrochromism: Fundamentals and Applications*, VCH Publishing, Weinheim, FRG (1995).
20. G.A. Sotzing and J.R. Reynolds, *Chem. Mater.*, **8**, 882 (1996).
21. S.A. Sapp, G.A. Sotzing, J.L. Reddinger and J.R. Reynolds, *Am. Chem. Soc., Div. Polym. Chem., Polymer Preprints*, **37** (1), 797 (1996).

22. J.D. Stenger-Smith, J.R. Reynolds, B. Sankaran, L.F. Warren, H.O. Marcy and G. Bauerele, *Proc. SPIE*, July 1995, San Diego, CA.